

198. *Mode of Proton Addition to Conjugated Double Bonds.*

By ALBERT WASSERMANN.

The light absorption and electrical conductance have been measured of vitamin-A acetate, a polyene with five conjugated double bonds, in benzene without and with trichloroacetic acid. The polyene is protonated in the presence of the acid; some information about the structure of the carbonium ion can be obtained.

In previous papers¹⁻³ the proton transfer from trichloroacetic acid to nine conjugated polyenes has been investigated, but in most cases the structure of the resulting carbonium ions has not been specified. It is now shown that another polyene, vitamin-A acetate, containing five conjugated double bonds, accepts protons, under conditions similar to those in the earlier experiments, and that the electronic spectrum of protonated vitamin-A acetate enables one to decide whether the proton goes to the middle part of the conjugated system or to its ends.

It is assumed that the proton transfer withdraws two π electrons from the conjugated double bonds and forms a new methylenic group as in the protonation of aromatic hydrocarbons.⁴

The product from trichloroacetic acid and vitamin-A acetate, prepared as specified below, is blue and characterised by a light absorption peak at 650 m μ . That vitamin-A acetate, or the vitamin itself, can be converted into deeply coloured substances is known,

¹ Wassermann, *J.*, 1954, 4329.

² *Idem*, *J.*, 1955, 581.

³ *Idem*, *J.*, 1958, 1014.

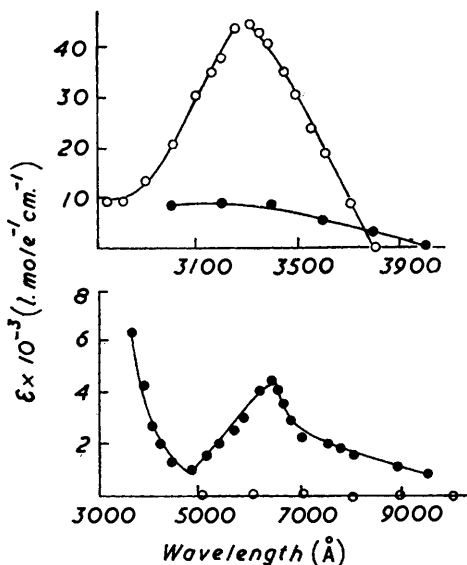
⁴ See, e.g., Dalinga, Mackor, and Veerijn Stuart, *Mol. Phys.*, 1958, **1**, 123, where are to be found references to earlier work.

the Carr-Price reaction, for instance, having been used for the colorimetric determination of the vitamin in biological materials.⁵ It is not known, however, whether the previously described coloured derivatives of vitamin-A are similar species to the carbonium-ion pairs which form the subject of this paper.

EXPERIMENTAL

The purifications and technique have been described.¹ Vitamin-A acetate, m. p. 57°, was recrystallised from methanol. Most of the spectrophotometry was done with a special all-silica cell, of small optical path-length, 0.0944 cm., suitable for relatively concentrated solutions.

FIG. 1. Light absorption of vitamin-A acetate in benzene solution at 20°.

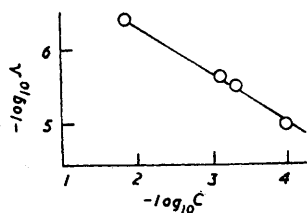


Concn. of vitamin-A acetate = 1.84×10^{-4} to 1.50×10^{-3} mole/l. ○ = No acid. ● = 0.920M-Trichloroacetic acid.

This is important because the rate of change of the optical densities, owing to a reaction with molecular oxygen, increases with decreasing polyene concentration. Back extrapolation of optical densities and of electrical conductances to the time of mixing was carried out.¹⁻³ The optical densities of solutions containing protonated vitamin-A acetate depend also on the intensity of illumination, this photochemical effect probably being similar to that with other carbonium ions,⁶ so all experiments were done in diffuse daylight of approximately equal intensity and the time of exposure to the light of the spectrophotometer (Unicam S.P. 500) was as short as possible.

Results.—The light absorption of vitamin-A acetate (Fig. 1) is markedly altered on addition of trichloroacetic acid, owing to proton-transfer. The equilibrium constant, K , relating to the proton uptake was obtained by plotting $\log K'$ (K' defined as in ref. 1) against trichloroacetic acid concentration and by extrapolating to zero concentration; K was so estimated to be 0.10 ± 0.02 l./mole in benzene at 20°. In these experiments the highest acid concentration was 3.96 moles/l. [here and below all concentration of trichloroacetic acid relate to the stoichiometric molecular weight]; at about half this concentration the optical density at 6500 Å had reached its limiting value. Measurements with different polyene concentrations were carried out, and the $\log K'$ values were extrapolated in each case to $[\text{CCl}_3 \cdot \text{CO}_2\text{H}] = 0$. The results of these

FIG. 2. Molar electrical conductance, Λ , of ion pairs formed by proton transfer from trichloroacetic acid to vitamin-A acetate.



Benzene solution, 25.0°. Ordinate: $-\log_{10} \Lambda$ (Λ in l. mole⁻¹ ohm⁻¹ cm.⁻¹); abscissa: $-\log_{10} c$ (c is concn. of ion pairs in mole l.⁻¹). The solution was 1.00M with respect to trichloroacetic acid.

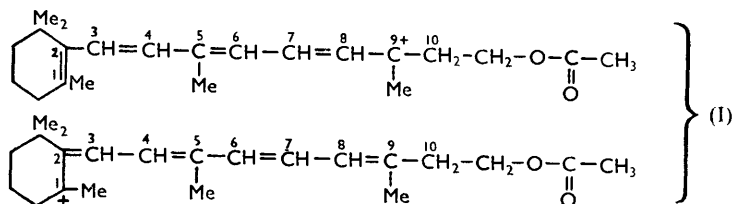
⁵ See, e.g., Gstirner, "Chem. Phys. Vitaminbestimmungsmethoden," Enke, Stuttgart, 1950; Moore, "Vitamin A," Elsevier, Amsterdam, 1957, chap. 7.

⁶ Reid, *J. Amer. Chem. Soc.*, 1954, **76**, 3264.

the upper limit of λ_1 , so obtained, is compared with the experimentally observed light absorption peak, shown in the lower part of Fig. 1 (these considerations relate to the wavelength of the peak; light-absorption intensities are not discussed here). The chromophore lengths were calculated from eqn. (2) (cf. Kuhn^{7,9})

$$L = Xl_1 + 2l_2 \dots \dots \dots (2)$$

where X depends on the position of the new methylenic grouping, and l_1 and l_2 are taken to be 1.39 and 1.50 Å. These values are probably somewhat too large, but as only upper



limits of λ_1 are calculated, the conclusions are not affected. If l_2 is also taken to be 1.39 Å, λ_1 for protonation in the 1- or the 10-position becomes 3% smaller. The figures in the last

Proton taken up by carbon atom no.	No. of formal double bonds in mesomeric part of protonated species	X or N *	L (Å) *	No. of ordinary conjugated double bonds in protonated species	$\lambda_1 \times 10^{-8}$ in Å (upper limits calc. from 1)
1 or 10	4	8	14.1	0	7.30
2 or 9	—	—	—	4	—
3 or 8	3	6	11.3	0	6.04
4 or 7	1	2	5.78	3	3.67
5 or 6	2	4	8.56	2	4.84

* These parameters relate to the mesomeric part of the protonated species.

column of the Table show that only the λ_1 value in the first line relating to 1- or 10-addition is larger than the experimental figure of 6500 Å. If the proton is transferred to the 2- or the 9-position, a mesomeric ion is not formed, the resulting carbonium ion containing four conjugated double bonds of the same type as those in the polyene before protonation. Such double bonds are also present in the species formed by 4- or 7- and 5- or 6-addition, which is indicated in col. 5 of the Table. These double bonds, in contrast to the formal double bonds in the mesomeric part of the protonated polyene, cannot give rise to light-absorption peaks above 3000 Å.¹⁰ The experimentally determined light-absorption curve makes it probable, therefore, that the proton uptake by vitamin-A acetate leads to the mesomeric ion with the maximum number of formal double bonds.

Discussions with Professors D. P. Craig and H. Kuhn are gratefully acknowledged.

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON, W.C.1.

[Received, August 19th, 1958.]

¹⁰ This follows, for instance, from a comparison with suitable reference substances; see *e.g.*, Naylor and Whiting, *J.*, 1955, 3037.